

Claims

1. An apparatus for measuring hydrogen concentration, comprising a proton-conducting solid electrolyte in conjunction with, or in contact with, a self-contained, sealed, metal/hydrogen reference standard, of which the content and/or the spatial distribution of oxygen is predetermined to render the solid electrolyte substantially chemically stable in the presence of the reference material.
- 10 2. An apparatus according to claim 1, wherein the proton conductor is a perovskite.
3. An apparatus according to claim 2, wherein the proton conductor is doped calcium zirconate or doped strontium cerate.
- 15 4. An apparatus according to any preceding claim, wherein the metal/hydrogen reference standard comprises titanium, zirconium or hafnium.
5. An apparatus according to any preceding claim, wherein the metal/ hydrogen reference standard has a metal with a metal to hydrogen atomic ratio such that two phases of the metal/hydrogen solution are present.
- 20 6. An apparatus according to claim 5, wherein the two-phase area is that of α -titanium/ β -titanium, α -zirconium/ β -zirconium, β -zirconium/ δ -zirconium, or α -hafnium/ δ -hafnium.
- 25 7. An apparatus according to claim 1, wherein the metal/hydrogen mixture has a bulk oxygen content that

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is sufficiently high to prevent reaction between the solid electrolyte and the reference material.

8. An apparatus according to claim 1, wherein the metal/hydrogen mixture is solid and is surrounded by an oxygen rich layer or comprises an oxygen-rich layer at its surface that prevents reaction between the solid electrolyte and the reference material.
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9. An apparatus according to claim 8, wherein the oxygen-rich layer on the solid reference material either originates from the production process of the metal or is generated subsequently by means of a chemical reaction.
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10. An apparatus according to claim 9, wherein the chemical reaction to generate an oxygen rich layer on the particles of a solid reference material consists in heating the metal of the reference system or the metal/hydrogen reference mixture in the presence of a metal oxide.
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11. An apparatus according to claim 1, wherein the solid electrolyte is coated with a catalyst at the point of contact with the electrode.
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12. An apparatus according to claim 11, wherein the catalytic coating is platinum.
13. An apparatus according to claim 1, wherein the sealing material is chemically stable in a hydrogen containing gas at elevated temperatures.
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14. An apparatus according to claim 13, wherein the sealing material is a silicon-free oxide glass that comprises one or more of the oxides of aluminium,

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barium, boron, calcium and/or magnesium, and
optionally has a melting temperature below 1200°C.

- 5 15. An apparatus according to claim 1, wherein an inert packing material is used as a separator between the reference and the sealing material.
16. An apparatus according to claim 15, wherein the inert packing material is calcium zirconate or yttrium oxide.
- 10 17. An apparatus according to claim 1, wherein the reference is created in two steps by, firstly, hermetically sealing the metal into the reference compartment and, secondly, passing hydrogen electrochemically through the solid electrolyte to form the metal/hydrogen reference.
- 15 18. An apparatus according to claim 1, wherein the metal/hydrogen reference is generated in one step, by heating the metal in the presence of a hydrogen containing gas while simultaneously forming a seal to close the reference compartment.
- 20 19. An apparatus according to any of the preceding claims, wherein the sensor, after preparation and prior to use, is preconditioned with a humidified gas of low hydrogen content at elevated temperatures.
- 25 20. An apparatus according to claim 19, wherein the preconditioning is performed in a humidified mixture of 1% hydrogen or less in argon at 700°C or more for 15 min or more.

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21. A method for measuring hydrogen concentration comprising the steps of; providing a probe comprising a proton-conducting solid electrolyte in conjunction with a sealed, or self-contained, hydrogen reference standard, in which the electrolyte is substantially stable in the presence of the reference standard; bringing the electrolyte into contact with a hydrogen concentration to be measured; and measuring a voltage generated across the electrolyte between the hydrogen concentration and the reference standard.
22. A method for making a metal/hydrogen reference standard for an apparatus comprising the reference standard in conjunction with a proton-conducting solid electrolyte, comprising the steps of; sealing the reference standard into a reference compartment; and passing hydrogen electrochemically through the solid electrolyte to form the reference standard.
23. A method for making a metal/hydrogen reference standard for an apparatus comprising the reference standard in conjunction with a proton-conducting solid electrolyte, comprising the step of; while sealing the reference standard into a reference compartment, heating the metal in the presence of a hydrogen-containing gas.
24. A probe substantially as described herein, with reference to the drawings.
25. A method for measuring a hydrogen concentration substantially as described herein.

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26. A method for making a metal/hydrogen reference standard substantially as described herein.